

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 September 2002 (12.09.2002)

PCT

(10) International Publication Number
WO 02/070425 A1

(51) International Patent Classification⁷: C04B 22/06 (81) Designated States (*national*): AE, AG, AL, AM, AT, AT // 103:12 (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EC, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/IB02/01833

(22) International Filing Date: 4 March 2002 (04.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/273,762	5 March 2001 (05.03.2001)	US
60/273,766	5 March 2001 (05.03.2001)	US
60/273,764	5 March 2001 (05.03.2001)	US
60/273,761	5 March 2001 (05.03.2001)	US

(71) Applicant (*for all designated States except US*): JAMES HARDIE RESEARCH PTY LIMITED [AU/AU]; Level 1, Research and Product Development Building, 10 Colquhoun Street, Rosehill, New South Wales 2142 (AU).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): JIANG, Chongjun [AU/AU]; 49 Waverly Street, Belmore, New South Wales 2192 (AU).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

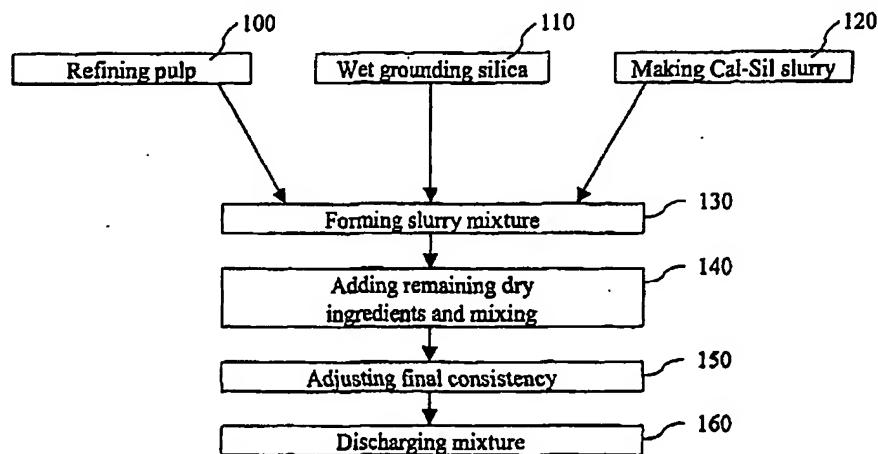
Published:

— *with International search report*

[Continued on next page]

(54) Title: LOW DENSITY CALCIUM SILICATE HYDRATE STRENGTH ACCELERANT ADDITIVE FOR CEMENTITIOUS PRODUCTS

WO 02/070425 A1



(57) Abstract: Disclosed are concrete and fiber cement formulations and products comprising low-density calcium silicate hydrate, and methods for producing these formulations and products. The disclosed formulations exhibit accelerated curing times. Other advantages of the disclosed formulations include improved dimensional stability in extruded products, reduced cracking, and reduced wash-out in underwater applications. The products of the disclosed formulation have lower cost of production and faster time to market.

WO 02/070425 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

LOW DENSITY CALCIUM SILICATE HYDRATE STRENGTH ACCELERANT ADDITIVE FOR CEMENTITIOUS PRODUCTSField of the Invention

The present disclosure relates to cementitious formulations, products, and methods of preparing the same, and in particular, cementitious formulations with accelerated curing.

Background of the Invention

Despite advances in the production of early-setting, high-strength cements, the development of Portland-type cements with even greater compressive strengths and higher rates of strength development would be highly beneficial to the cement and the construction industries. For example, producing pre-cast, pre-stressed, concrete products with compressive strengths on the order of 4000–5000 psi often requires at least three hours or more.

Additionally, the construction and repair of highways, bridges, and freeway overpasses requires many days and even weeks of curing time before these structures set to sufficient compressive strengths to support their anticipated loads so that they may be utilized as designed. The resulting delays are a significant component of construction costs, which are compounded by increased transportation costs and shipping delays while critical transportation corridors are shut down waiting for concrete to harden.

Moreover, in the construction of concrete buildings, in which the cement matrix is cast into forms, days of curing time are necessary to allow the cement to develop sufficient strength before the forms may be removed. Such delays result in lost revenues for property owners, as well as inconvenience and storage costs for industrial tenants. Furthermore, setting rates of Portland-type cements can be affected by temperature. An early setting, ultra-high strength cement with a lower heat of hydration would make the production of large, complex superstructures possible at low ambient temperatures and would be an even greater contribution to the construction industry.

Many cement-based products are also mass manufactured in high-throughput factory situations. The time that it takes for cement to cure or set completely adds to the cost and difficulty of manufacturing. In particular, fiber cement products are manufactured in this way, by processes such as the Hatschek process, the Mazza process, or by extrusion. When a fiber cement product is formed in its “green” state, it typically must set for 8 to 12

hours ("precure") before additional processing or handling can occur. Precuring requires warehouse space as green products accumulate while setting, which adds to the cost of the manufacturing process. Consequently, there is a strong business motivation to reduce the curing time of cement, and in particular, fiber cement materials. Furthermore, methods of reducing the curing time at a substantially lower cost than conventional quick-setting cement formulations, such as high alumina cement, are very desirable.

The best-known and most commonly used accelerant for setting cement is calcium chloride. However, it is widely known in the art that calcium chloride is incompatible with steel-reinforced cements due to its tendency to corrode the steel reinforcement over time in the presence of water and oxygen. Calcium chloride is also sometimes used as an accelerant in fiber cement manufacturing to obtain green strength quickly; however, buildup of chloride ions can also cause corrosion problems in downstream manufacturing processes such as autoclaves. Accordingly, an accelerant for setting concrete and cement composites that does not cause corrosion is needed.

Besides calcium chloride, other accelerants, such as alkaline bases (sodium hydroxide, potassium hydroxide, ammonia, sodium or potassium carbonate, and sodium or potassium silicate), alkaline or alkaline earth metal nitrates, nitrites or carboxylates are all chloride-free with reduced corrosiveness compared to calcium chloride. However, these materials must still be added separately to concrete or cement composite formulations and thus require their own storage vessels, metering apparatus, and mixing/blending processes, either manual or automated, to incorporate them into a composite. On the other hand, it is well known that low-density modifiers for concrete, such as perlite or ceramic microspheres, do not accelerate cement hydration. A single material that provides both an accelerated curing effect and some other desirable function, such as density reduction, in a concrete or cement composite would save considerable time and equipment capital.

There are several well-known organic materials used in cementitious composites and concrete applications. These so called admixtures include cellulose ethers for rheology modification, lignosulfonate or naphthalene sulfonates as water reducing agents and superplasticisers, polymer latexes or emulsions for modifying water absorption properties or improving flexibility, as well as other organic admixtures well known in the art. One typical effect of these admixtures is retarding the setting time of the cement. Often, an accelerant is used to counteract this retarding effect. Accelerants known in the art are

corrosive and/or expensive relative to ordinary Portland cement and can add significant cost to a concrete or cement composite formulation.

LeTure et al., in U.S. Patent Number 5,709,743 disclose a calcium silicate hydrate based accelerator that does not cause corrosion and is as effective as calcium chloride. This material is prepared by hydrating Portland cement to form a calcium silicate hydrate (CSH) material. This CSH material is then finely ground into "crystallization seeds" which accelerate the cure of cement cubes when added in an aqueous suspension to cement. Grinding or milling the calcium silicate particles to a specific particle size (as determined by sedimentation volume) is a crux of the invention described in 5,709,743. Grinding or milling such particles inherently increases their packing density and thus CSH particles made according to the disclosure of LeTure et al. are unsuitable as a low-density additive.

Another drawback of using the CSH accelerator of LeTure et al. is that it must be added as aqueous slurry. This is a disadvantage for cement composite mixes, such as extrudable cement composites in which the water content is carefully managed to ensure consistent product quality.

One way to achieve green strength quickly in concrete is to use "high early strength" cement, which is ground to a finer particle size and has greater surface area (450 to 600 m²/kg, Blaine method) than standard Portland cement (300 to 400 m²/kg). These fine cements are not suitable for use in the Hatschek process typically used to make fiber cement composites because the fine cement is not retained in the composite during the slurry dewatering process.

In fiber cement manufacture, low-density additives often reduce the strength-to-weight ratios of the fiber cement. Since building materials must meet specific strength criteria, this effect limits the amount of low-density material that can be used in a fiber cement composite.

When a green fiber cement paste is extruded under pressure through a die, the green uncured fiber cement paste tends to "springback" after leaving the extrusion die. The degree of springback is a function of the cement paste rheology, processing history, fiber content and type, air entrainment, and other factors well known in the art. One way to reduce springback is to increase the length of the die, allowing the green fiber cement paste more time to "relax" in its compressed state. However, longer dies are more expensive than shorter dies, and longer dies tend to increase the pressure required to extrude the fiber

cement paste. High-pressure extrusion can damage fragile low-density aggregates used in the paste, so a low cost material additive would be a better solution.

Forming concrete underwater, either for repair of existing structures or the building of new structures, often results in the "washout" of fines from the freshly mixed concrete and/or in segregation of the concrete mix. Consequently, most concrete mixes used for underwater placement include a high viscosity cellulose ether material as an anti-washout admixture. However, where large amounts of concrete need to be placed in areas with severe water flow and/or water pressure, such as repair of dams and back filling the annular void behind tunnel linings, the cellulose based anti-washout admixtures can be ineffective in completely preventing washout and segregation, mainly due to its extended delay in cement hydration.

Summary of the Invention

A first embodiment of the invention provides a low-density calcium silicate hydrate accelerator and strength-enhancing agent for concrete and cement composites, including fiber cement. A second embodiment provides a method of using the low-density calcium silicate hydrate accelerator in Hatschek fiber cement formulations and products. A third embodiment provides a method of using the low-density calcium silicate hydrate accelerator in extruded fiber cement. A fourth embodiment provides a fiber cement formulation containing a low-density calcium silicate hydrate accelerator. A fifth embodiment provides a concrete formulation containing a low-density calcium silicate hydrate accelerator. A sixth embodiment provides a method of using a low-density calcium silicate hydrate to prepare a concrete mixture. A seventh embodiment provides a method accelerating the curing of concrete and cementitious composites, including fiber cement, using low-density calcium silicate hydrate.

As used herein, "CSH" refers to "calcium silicate hydrate," "LD-CSH" refers to "low-density calcium silicate hydrate," also referred to as "low-density CSH." "OPC" refers to "ordinary Portland cement." "FC" refers to "fiber cement" and "FRC" refers to "fiber-reinforced cement," and the two are used interchangeably. The term "Portland cement" includes, but is not limited to, ordinary Portland cement, off-white Portland cement, and blended cement. Cellulose fiber may be hardwood, softwood, or non-wood cellulose fibers. Unless otherwise noted, all percentages are by weight.

Preferred embodiments disclosed herein use a low-density calcium silicate hydrate accelerant for simultaneously reducing both the density and the curing time while enhancing the strength to weight ratio of concrete and cement-containing composites, especially fiber cement.

The low-density calcium silicate hydrate material disclosed herein can be made according to the methods given in U.S. Patent No. 6,346,146. Commercially available, synthetic low-density calcium silicate hydrate materials, such as Celite Micro-cel® A or E (World Minerals, Lompoc, CA; used as a filter aid, absorbing agent, and agrochemical carrier) are also useful as low-density accelerants for concrete and cement composites as disclosed herein.

Low-density CSH accelerant has a bulk density of about between 0.015 g/cm³ and 1.5 g/cm³ (15 kg/m³ to 1500 kg/m³). It is equally effective when added to concrete or cement, including fiber cement, composite as a dry powder or as slurry. The low-density CSH has an accelerating effect when added to fiber cement or concrete on a weight basis of about 0.5% to 50%, and more preferably between about 5% and 15% by weight. Preferably, the curing time is accelerated by about 10% or more compared to an equivalent product or formulation made without low-density calcium silicate hydrate. More preferably, the acceleration is about 20% or more. In fact, curing accelerations of about 30%, 40%, 50%, 60%, 70%, or even 80% or more may be realized by incorporating an appropriate amount of low-density CSH.

When used in extrudable fiber cement pastes, low-density CSH overcomes the retarding effects of organic admixtures by accelerating the set time of the fiber cement paste. Low-density CSH overcomes the retarding effects of organic admixtures when added to extrudable fiber cement pastes at levels between 2% and 20% by weight, more preferably between 5% and 15% by weight.

When used in extrudable fiber cement pastes, the low-density CSH also counteracts post-die swelling of the extruded material by accelerating the set time of the fiber cement paste. Low density CSH is effective at reducing post-die swelling when added to extrudable fiber cement pastes at levels between about 2% and 20% by weight, more preferably between about 5% and 15% by weight.

When used to formulate fiber cement composites, low-density CSH enables the production of material with lower density (about 0.6 g/cm³ to 1.2 g/cm³) than traditional

fiber cement, with improved strength-to-weight ratio versus fiber cement made without low-density CSH. This effect is observed when low-density CSH is added to fiber cement composites in a range of about 3% to 20%, more preferably in the range of about 3% to 15%.

The low-density calcium silicate hydrate of the preferred embodiments does not contain appreciable amounts of chloride ion. Accordingly, it will not have the corrosive properties of calcium chloride. The low density CSH of the preferred embodiments forms coarse agglomerates in water making it readily retained in wet-process fiber cement operations such as the Hatschek process.

Brief Description of the Drawings

FIGURE 1 illustrates a method of making a fiber cement mixture with LD-CSH for the Hatschek process.

FIGURE 2 illustrates a method of making a concrete mixture with LD-CSH for construction applications.

FIGURE 3 illustrates a method of making a cementitious mixture with LD-CSH for extruded FRC applications.

FIGURE 4 illustrates the curing behavior of fiber cement formulations containing low-density calcium silicate hydrate (LD-CSH).

Detailed Description of the Preferred Embodiments

Disclosed herein are cementitious formulations comprising low-density calcium silicate hydrate, products made with these formulations, and methods of making such formulations and products. These formulations and methods are advantageously used, for example, in the Hatschek production process, and in construction applications such as building, road, and bridge repair and construction. Such formulations are also useful in underwater applications where they also exhibit reduced washout. Because the disclosed formulations exhibit reduced setting times and reduced cracking, the cementitious products of these formulations often have lower costs and improved time to market.

Fiber cement mixtures comprising between about 0.5% and 15% by weight low-density calcium silicate hydrate (LD-CSH) curing accelerator are advantageously used in the Hatschek production process. Preferably, the mixture comprises between about 25% and 50% cement, between about 25% and 50% silica ground to about 200-mesh, between about 0% and 15% aggregate, between about 5% and 15% cellulose fiber, between about 0% and

5% additives, between about 0.5% and 15% low-density calcium silicate hydrate, and water. The total water content depends on the consistency required by the Hatschek process. Fiber cement products manufactured from this mixture may have lower-cost, reduced curing times, reduced cracking when curing, and improved time to market. Preferred fiber cement formulations comprising low-density calcium silicate hydrate for use in the Hatschek process are provided in TABLE 1.

TABLE 1

Ingredient ^a	Range	Example
Cement	25-50%	42%
Silica	25-50%	33%
Aggregate	0-15%	0%
Cellulose fiber	5-15%	11%
Additives	0-5%	3%
Low-density CSH	0.5-15%	11%

^a Proportions by wt%.

The following ingredients exemplify one preferred embodiment. The cement is ordinary Portland cement to the specifications currently used by conventional Hatschek factories. The silica is 200-mesh ground silica. Preferably, the aggregate is any siliceous aggregate, for example, cenospheres, perlite, fly ash, bottom ash, etc. with particle size ranging from about 50 to 250 microns. The cellulose fiber is, for example, hammer-milled Kraft pulp. The moisture content of the pulp at ambient conditions (approximately 9%) should be taken into account when batching the water. Additives include any compound required to achieve desired properties of the mixture, for example alumina. The low-density CSH is Micro-cel E (World Minerals, Lompoc, CA) or the LD-CSH prepared according to EXAMPLES 1 or 2 below. The total water content required depends on the desired consistency of the formulation. For the Hatschek process, typically a slurry of about 5% to 10% solids content provides good processability.

It will appreciated that the cementitious binder, in addition to Portland cement, can also be, but is not limited to, high alumina cement, lime, high phosphate cement, and ground granulated blast furnace slag cement, or mixtures thereof. The aggregate may include, but is not limited to, ground silica sand, amorphous silica, micro-silica, diatomaceous earth, coal combustion fly and bottom ash, rice hull ash, blast furnace slag, granulated slag, steel slag, mineral oxides, mineral hydroxides, clays, magnesite or dolomite, metal oxides and hydroxides, and polymeric beads, mixtures thereof, and other

aggregates described above and below. The additives can include, but are not limited to, viscosity modifiers, fire retardants, waterproofing agents, silica fume, geothermal silica, thickeners, pigments, colorants, plasticizers, dispersants, forming agents, flocculents, drainage aids, wet and dry strength aids, silicone materials, aluminum powder, clay, kaolin, alumina trihydrate, mica, metakaolin, calcium carbonate, wollastonite, and polymeric resin emulsion, and mixtures of thereof or other materials.

The cellulose fibers are unrefined/unfibrillated or refined/fibrillated cellulose pulps from various sources, including but not limited to bleached, unbleached, semi-bleached cellulose pulp. The cellulose pulps can be made of softwood, hardwood, agricultural raw materials, recycled waste paper or any other forms of lignocellulosic materials. Cellulose fibers can be made by various pulping methods. In the pulping process wood or other lignocellulosic raw materials such as kenaf, straw, and bamboo, etc., are reduced to a fibrous mass by the means of rupturing the bonds within the structures of lignocellulosic materials. This task can be accomplished chemically, mechanically, thermally, biologically, or by combinations of these treatments. The cellulose fibers used for reinforcing cement composite materials in one embodiment are predominantly individualized fibers with partial or complete removals of lignin components from the fiber cell walls.

Fiber cement mixtures comprising between about 0.5% and 15% by weight low-density CSH are prepared by a method comprising preparing refined pulp slurry; wet grounding silica sand to form a silica slurry; making an low-density CSH slurry; forming a slurry mixture from the above slurries; adding other dry ingredients, such as cement, aggregates, and additives; and adjusting final consistency by adding water as required and mixing.

FIGURE 1 illustrates a preferred method of making a fiber cement mixture comprising low-density calcium silicate hydrate for the Hatschek process. In step 100 ("Refining pulp"), lap type of cellulose fiber pulp is hydrated and refined using a pulp refiner, forming a slurry of refined pulp with a consistency of about 5% to 7%. The slurry is batched in step 130. In step 110 ("Wet grounding silica") silica sand is wet ground using a ball mill to produce a fine silica slurry of approximately 50% consistency. The slurry is batched in step 130. Step 120 ("Making LD-CSH slurry") provides a low-density CSH slurry. Low-density CSH may be prepared in-situ or purchased commercially as a dry powder. Where the low-density CSH is made in-situ, a slurry is typically supplied from the

manufacturing section, which is batched in step 130. Where the low-density CSH is dry, for example, CSH purchased commercially, the dry CSH is typically batched and mixed in step 140. In step 130 ("Forming slurry mixture"), the fiber slurry from step 100, the silica slurry from step 110, and the LD-CSH slurry from step 120 are batched according to the required amount as provided in TABLE 1 and added into the mixing tank. The moisture content of the mixture is measured, and the amount of water added in step 150 is adjusted to compensate. In step 140 ("Adding remaining dry ingredients and mixing"), the remaining solid ingredients, for example cement, aggregates, additives, and low-density CSH (if using dry CSH) are weighed out according to TABLE 1 and add into the mixing tank. In step 150 ("Adjusting final consistency"), the solid content of the slurry from step 140 is measured. Additional water may be added to achieve the desired consistency. The resulting slurry is then mixed thoroughly to generate a slurry suitable for sheet formation. In step 160 ("Discharging mixture"), the slurry mixture is discharged and pumped into the sheet formation section, for example, into tubs.

Cementitious mixtures comprising between about 0.5% and 20% by weight low-density calcium silicate hydrate are useful in construction applications, such as construction, road and bridge repair, as well as for underwater applications. Preferably, the cementitious mixture comprises between about 15% and 50% cement; between about 0% and 70% silica, where the silica is quartz sand of about 100 to 400 microns particle size; between about 0% and 40% aggregate; between about 0% and 15% fiber; between about 0% and 2% additives; between about 0% and 0.2% leveling agent; between about 0% and 2% water reducing agent; between about 0% and 1% aeration agent; between about 0.5% and 20% low-density calcium silicate hydrate; and water. The total water content is usually determined by the required water to cement ratio (W/C) for the given application, preferably in a range between about 0.35 and 1. Cementitious products made from this cementitious mixture may have lower-cost, reduced curing times, reduced cracking when curing due to excessive shrinking and high heat of hydration, reduced time to market, and reduced washout in underwater forming applications. Preferred formulations for cementitious mixtures comprising low-density CSH for construction applications are provided in TABLE 2.

Table 2

Ingredient ^a	Range	Example
Cement	15-50%	37.66%
Silica	0-70%	46.04%
Aggregate	0-40%	10%
Fiber	0-15%	0%
Additives	0-2%	1%
Leveling Agent	0-0.2%	0%
Water Reducing Agent	0-2%	0.3%
Aeration Agent	0-1%	0%
Low-density CSH	0.5-20%	5%

^a Proportions by wt%.

The following ingredients exemplify one preferred embodiment. The cement is ordinary Portland cement to the specifications currently used in conventional construction applications, such as road paving and bridge construction. The silica is, for example, quartz sand of particle size from about 100 to 400 microns. Preferably, the aggregate is any siliceous aggregate, for example, gravels, limestone, bottom ash, etc. of particle size up to about 20 mm. Fiber reinforcement is used in some construction applications depending on the desired properties of the concrete. For example, steel wire or rods, poly-fiber, and carbon fiber are often used in the construction of foundations, bridges, and underwater structures. Additives include any compounds required to achieve desired properties in the mixture, for example, viscosity-enhancing agents (VEAs) for an appropriate water-retention ability and deformability. Examples of VEAs are methylcellulose, hydroxyethylcellulose, hydroxyethylmethylcellulose and hydroxypropylmethylcellulose. Leveling agents are used in self-leveling applications, for example for floors. Examples are Clariant Tylose MH and H. Water reducing agents are, for example, any superplasticiser of the sulfonated melamine formaldehyde (SMF) condensate, sulfonated naphthalene formaldehyde (SNF) condensate, or acrylic polymer (AP) families. Aeration agents are also called air entrainment agents (AEAs), such as AE4. The low-density CSH is Micro-cel E (World Minerals, Lompoc, CA) or the LD-CSH prepared according to EXAMPLES 1 or 2 below.

The total water content is adjusted to provide a mix with the desired properties, for example, fluidity and workability. For typical applications, the water to cement ratio (W/C), is preferably in a range of between 0.35 and 1, more preferably 0.45.

These cementitious mixtures comprising between about 0.5% and 20% by weight low-density calcium silicate hydrate for use in construction applications are prepared by a method comprising combining cement, silica, aggregates, additives, and a water reducing agent; dry mixing the ingredients; adding water; mixing; and adding low-density calcium silicate hydrate. In a preferred embodiment, the method further comprises adding fiber, a leveling agent, or an aeration agent, either alone or in combination.

FIGURE 2 illustrates an exemplifying method of making cementitious mixtures comprising low-density CSH for construction applications. In step 200 ("Adding solid ingredients, except LD-CSH"), cement, silica, aggregates, fiber, additives, leveling agent, water reducing agent, and aeration agent are weighed-out according to **TABLE 2** and added into a mixing machine such as a Hobart mixer. In step 210 ("Dry mixing the ingredients"), the dry ingredients are dry mixed in the mixing machine for a predetermined time, preferably about 1 to 5 minutes. In step 220 ("Adding water"), water is added to the mixture. The amount of water added depends on the consistency required for the particular application. The total water content required to give the desired properties, such as fluidity and workability, is usually determined by the water to cement ratio, W/C, preferably between about 0.35 and 1, more preferably about 0.45. When the batching water is calculated, it is necessary to determine the amount water already present in the solid ingredients, for example in step 200, and subtract that amount. The temperature of the mixture is preferably lower than about 45 °C, more preferably about 25 °C. The particular temperature depends on factors including the amount of LD-CSH in the mixture, and the type and quantities of other additives such as cellulose ether. In step 230 ("Mixing"), the formulation in the mixing machine is mixed for a predetermined period of time, preferably about 1 to 5 minutes. The temperature of the mixture is preferably lower than about 45 °C, more preferably about 25 °C. The particular temperature depends on factors including the amount of low-density CSH in the mixture, and the type and quantities of other additives such as cellulose ether. Near the expected time of use, in step 240 ("Adding LD-CSH"), low-density CSH is weighed-out according to **TABLE 2** and added to the mixing machine. The formulation is mixed in the mixing machine for a predetermined period of time, preferably about 1 to 5 minutes. The length of time between the addition of the low-density CSH to the mixture (including the mixing time) and the expected time of use must be less than the setting time of the mixture. Accordingly, to prevent the mixture from setting in the

truck, the CSH may be added to the mixture using a portable mixing machine at the construction site. The temperature of the mixture is preferably lower than about 45 °C, more preferably between about 25 to 30 °C. The particular temperature depends on factors including the amount of low-density CSH in the mixture, and the type and quantities of other additives such as cellulose ether. Under high temperature conditions, for example in hot weather, the temperature of the mixture may be controlled by replacing a portion of the water with, for example, ice. In step 250 ("Discharging Mixture"), the mixture is discharged, for example, into construction forms.

FIGURE 3 illustrates an example method of making cementitious mixtures comprising low-density CSH for FRC extrusion applications. In step 300 ("Adding solid ingredients including LD-CSH (if supplied dry)"), cement, silica, aggregate, fiber, additives, water reducing agent, and other additives are weighed-out according to TABLE 3 and added into a mixing machine such as an Birich mixer. In step 310 ("Dry mixing the ingredients"), the dry ingredients are dry mixed in the mixing machine for a predetermined time, preferably about 1 to 5 minutes. In step 320 ("Adding water including silica and LD-CSH (if supplied in slurry)"), water is added to the mixture. The amount of water added depends on the consistency required for the particular application. The amount should be adjusted according to the water content of any silica and LD-CSH slurry if supplied in slurry. The total water content required to give the desired properties, such as fluidity and workability, is usually determined by the water to solid ratio, W/S, preferably between about 0.4 and 1.2, more preferably between about 0.48 and 0.8. When the batching water is calculated, it is necessary to determine the amount water already present in the solid ingredients, for example in step 300, and subtract that amount. The temperature of the mixture is preferably lower than about 45 °C, more preferably about 25 °C. The particular temperature depends on factors including the amount of LD-CSH in the mixture, and the type and quantities of other additives such as cellulose ether. In step 330 ("Wet mixing ingredients"), the formulation in the mixing machine is mixed for a predetermined period of time, preferably about 1 to 5 minutes. In step 340 ("Discharging the material into the kneader and knead to paste"), the mixture is discharged into a kneader and kneaded for a certain period to form a dough-like paste. In step 350 ("Discharging the paste and transfer to the degassing section"), the paste is then discharged and transferred to the degassing section of the extruder for degassing under vacuum. In step 360 ("Extruding the degassed

pasted through a die"), the paste is fed into the extruder auger and extruded through a die to form a green product. In step 370 ("Pre-curing the green products at controlled conditions"), the green product is precured under controlled conditions for a certain period of time, preferably at about 50 °C and about 80% relative humidity. In step 380 ("Autoclaving the green products at saturated steam conditions"), products are loaded into an autoclave and steam-cured at about 180 °C for about 8 hours. In step 390 ("Finishing extruded FRC"), the products are finished with sanding or painting on the surface as required.

Table 3

Ingredient ^a	Range	Example
Cement	15–60%	44.5%
Silica	0–60%	29.7%
Aggregate	0–40%	10%
Fiber (including synthetic fiber)	0–15%	9%
Additives	0–2%	0%
Viscosity Enhancing Agent	0.2–3%	1.5%
Water Reducing Agent	0–2%	0.3%
Aeration Agent	0–1%	0%
Low-density CSH	2–20%	5%

^a Proportions by wt%.

The following ingredients exemplify one preferred embodiment. The cement is ordinary Portland cement to the specifications currently used by conventional extrusion processes. The silica is 200-mesh ground silica. Preferably, the aggregate may be any siliceous aggregate, for example, cenospheres, perlite, fly ash, bottom ash, etc., with particle size ranging from about 50 to 250 microns. Fibers may be cellulose fibers or synthetic polymer fibers. The cellulose fiber is, for example, hammer-milled Kraft pulp. The moisture content of the pulp at ambient conditions (approximately 9%) should be taken into account when batching the water. Additives include any compound required to achieve desired properties of the mixture, for example alumina. The low-density CSH is Micro-cel E (World Minerals, Lompoc, CA) or the LD-CSH prepared according to EXAMPLES 1 or 2 below. The total water content required depends on the desired consistency of the formulation.

EXAMPLE 1. Preparing low-density CSH.

Process lime water is weighed into the batch tank at a ratio of 6.0 L water per kg of lime (CaO) in the batch. It should be noted that the present example process is suitable for use with both fresh town water or process water. The water is discharged into the mixing tank and then heated with steam to about 65 °C. The steam adds extra water. A 1300 kg batch of raw materials requires about 628 kg of lime which is slaked in about 3767 L of lime water and about 672 kg dry weight of ground quartz sand in a slurry at about 40% solids which is added to the slaked lime in a stirred tank.

The ground quartz sand is prepared as follows. Quartz sand is ground in a vertical stirred ball mill to a particle size such that 90% of the volume of the silica has a diameter of less than about 11.6 microns as measured by a Malvern "Mastersizer" laser diffraction particle size analyzer.

The slurry is mixed for about 15 minutes then pumped into the stirred pressure vessel. Water is added to modify the viscosity of the slurry. The slurry is heated with steam to a pressure of about 700 ± 50 kPa. The reaction is maintained at this pressure by addition of steam into the vessel. The material is maintained at pressure for about 3 hours by further intermittent injections of steam. After about 3 hours at full pressure, the pressure is then blown-off to about 270 kPa in 30 minutes. The material is then discharged into a tank via a cyclone to allow the liberation of steam from the slurry. The slurry is then diluted with lime water to between about 10–12 wt% dry solids of low-density CSH product and pumped to a stirred storage tank.

EXAMPLE 2. Preparing low-density CSH with milled silica

The example below describes the conversion of lime and ground quartz silica into low-density CSH of predominantly the tobermorite phase with a reaction time of only about 2 hours with no greater than about 10% unreacted silica.

Silica sand of average particle size between 0.3 and 0.5 mm is ground in a vertical stirred ball mill to a particle size of about $D[90] = 8.84 \mu\text{m}$. $D[90]$ represents the particle diameter that 90% weight of silica is less than, as measured by a Malvern "Mastersizer" particle size analyzer.

The lime and milled silica are then mixed into an aqueous slurry in a stirred pressure vessel. The molar ratio of lime to silica is about 1:1. Water is added to give a dry solids concentration of $4\% \pm 1\%$. The reaction is heated from ambient to 170 ± 5 °C in

about 40 minutes with a steam pressure of 750 ± 50 kPa. The stirred pressure vessel is maintained under these conditions for about 2 hours.

Properties of the calcium silicate hydrate as synthesized in EXAMPLES 1 and 2 as well as commercially available CSH are provided below. TABLE 4 provides physical properties of various low-density CSH materials. TABLE 5 provides typical chemical analyses of low-density CSH materials.

TABLE 4

Property	CSH of Example 1	CSH of Example 2	Celite Micro-cel E®
Unreacted Silica	7.5%	4.1%	0.1%
Tamped Dry Bulk Density	217 kg/m ³	84 kg/m ³	18 kg/m ³

TABLE 5

Material	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O + K ₂ O	LOI ^a
CSH of Example 1	49	29	3	0.7	0.7	2.2	15
Micro-cel E	47	32	2.5	0.7	2.2	1.3	15

Percentages by weight. ^a Loss on ignition.

The use of low-density calcium silicate hydrate as an accelerator is illustrated in the following examples.

EXAMPLE 3. Accelerated cure of green fiber cement pastes

Three fiber cement pastes of equal dry density (about 0.85 g/cm³) were formed from ordinary Portland cement (OPC Type I, TXI), 200-mesh, ground silica, refined cellulose fiber (bleached kraft pulp, Weyerhaeuser), water, and a low-density additive. The low density additive – hollow ceramic microspheres and/or dry, low-density CSH (Micro-cel E®, World Minerals, Lompoc, CA) – was added to achieve the target density. To prepare the paste, 300 grams of the dry components proportioned according to TABLE 6 were mixed together in an Eirich R-02 high-shear mixer for about 3 minutes. Water was added to the mixture to form a paste, and the mixture was mixed for an additional 2 minutes. The paste was transferred to a Hobart-type mixer and kneaded for 2 to 3 minutes to further homogenize the paste. A sample of each paste was placed in a 200-mL plastic bottle and an RTD thermocouple was inserted in the mixture. The container was sealed and placed in a calorimeter (Calorimetre de Langvant) located in an incubating room held at 22 °C.

TABLE 6

Formulation	Portland Cement	200-mesh Ground Silica	Cellulose Fiber	Hollow Ceramic Spheres	Low-density CSH	Water ^a
A	39	39	11	0	11	71
B	39	39	11	6	5	64
C	39	39	11	11	0	56

Dry components by wt% of total dry weight. ^a Percent water added based on total weight of dry components to maintain consistent paste workability.

Temperature and time data were collected as each sample cured and are plotted in FIGURE 4. For each sample, the time of the maximum temperature (T_{max}) and the time of the maximum rate of temperature increase ($T_{maxrate}$) were recorded. As shown in TABLE 7, T_{max} decreased with increasing CSH, showing the accelerating effect of low-density CSH in fiber cement formulations. Formulation A (11% LD-CSH) reached T_{max} about 70% faster than formulation C (no LD-CSH). Formulation B (5% LD-CSH + ceramic spheres) reached T_{max} about 60% faster than formulation A. For $T_{maxrate}$, the values are about 80% faster for formulation A, and about 75% faster for formulation B.

TABLE 7

Formulation	T_{max} (hours) ^a	$T_{maxrate}$ (hours) ^b
A	9.5	3.6
B	11.2	4.9
C	30.1	19.9

^a Time of the maximum temperature. ^b Time of the maximum rate of temperature increase.

EXAMPLE 4. Accelerated cure of concrete formulations using low-density CSH

Concrete pastes, without fiber, were prepared according to TABLE 8. Portland cement (Blue Circle Southern), natural raw sand (0.24 mm to 4 mm), and high-range water reducer (HRWR, Melmet® F-15, SKW Chemical) were blended with either calcium chloride powder (AR grade, Aldrich Chemical) or dry, low-density CSH (Micro-cel E®, World Minerals, Lompoc, CA). The dry components were mixed in an Eirich R-02 mixer for about 1 minute, then transferred to a Hobart mixer and blended with water to achieve similar paste workability.

TABLE 8

Formulation	Portland Cement	Natural Raw Sand, 0.24–4 mm	HRWR	CaCl_2	LD-CSH	Water ^b
D	200	800	3	0	55	205
E	200	800	3	2	0	100
F	200	800	3	0	0	100

Quantities in grams. ^a High-range water reducer. ^b Water adjusted to maintain consistent paste workability.

Once mixed, a sample of each concrete paste formulation was placed in a 200-mL plastic bottle with an RTD thermocouple and the bottles placed in a calorimeter (Calorimetre de Langvant) located in a curing room at 22 °C. Time and temperature data were collected as described in EXAMPLE 3. TABLE 9 indicates that low-density CSH compares favorably to CaCl₂ with respect to accelerating the curing of concrete. Formulation D (5.1% LD-CSH) reached T_{max} about 65% faster than formulation F (no LD-CSH), and T_{maxrate} about 80% faster.

TABLE 9

Formulation	T _{max} (hours) ^a	T _{maxrate} (hours) ^b
D	10.5	5
E	19.5	15
F	31.3	25.4

^a Time of the maximum temperature. ^b Time of the maximum rate of temperature increase.

EXAMPLE 5. Effect of low-density CSH on cure behavior of extruded fiber cement with organic admixtures

Extrudable fiber cement pastes were prepared according to TABLE 10. Cement, silica, fiber, and calcium chloride were obtained from the sources listed in the previous examples. In these tests, organic admixtures VEA (a proprietary grade of methylhydroxyethylcellulose, Shin-Etsu Chemical) and DA (Melmet F-15, SKW Chemical) were added to improve the paste rheology and workability. The solid components were blended in a high-speed Eirich R-02 mixer and subsequently mixed with water in a Hobart mixer. The paste produced was then extruded as square edged sheets, 50 mm wide by 10 mm thick, using a Handlē laboratory extruder with a 75-mm barrel.

TABLE 10

Formulation	Portland Cement	200-mesh Ground Silica	Cellulose Fiber	VEA	DA	Hollow Ceramic Spheres	Low-density CSH ^a	Water ^b
G	41.7	27.8	9	1.5	0	20	0	56
H	41.5	27.7	9	1.5	0.3	20	0	56
I	39.7	26.5	9	1.5	0.3	20	3	56
J	39.9	26.6	9	1.5	0	20	3	56
G + 1 wt% CaCl ₂	41.7	27.8	9	1.5	0	20	0	56

Dry components by wt% of total dry weight. ^a Micro-cel® E. ^b Percent water added based on total weight of dry components to maintain consistent paste workability.

Paste setting times and temperatures were recorded as in EXAMPLES 3 and 4 using RTD thermocouples embedded in approximately 200 mL of the extruded paste. As shown in TABLE 11, 3% low-density CSH effectively accelerates the setting time of extrudable fiber cement pastes with relatively high loadings of organic admixtures. The magnitude of the acceleration is comparable to the effect of calcium chloride. Comparing formulations H (no LD-CSH) and I (3% LD-CSH), T_{max} was reached about 65% faster and $T_{maxrate}$ about 70% faster. For formulations G (no LD-CSH) and J (3% LD-CSH), the values are about 55% faster to T_{max} and about 60% faster to $T_{maxrate}$ for the LD-CSH containing formulation.

TABLE 11

Y	T_{max} (hours) ^a	$T_{maxrate}$ (hours) ^b
G	60	46
H	82	69.5
I	28	19
J	26	17
G +1wt% CaCl ₂	26.6	22

^a Time of the maximum temperature. ^b Time of the maximum rate of temperature increase.

EXAMPLE 6. Comparison of the acceleration effects of
the low-density CSH of EXAMPLE 1 to Micro-cel B

Extrudable fiber cement paste samples were prepared using the method described in EXAMPLE 5 according to the proportions of TABLE 12. Formulations containing equal amounts of the low-density CSH prepared in EXAMPLE 1 and Micro-cel B were compared to a formulation containing no low density CSH. Extruded planks, 89 mm wide by 25 mm thick, of each formulation were placed in a curing chamber maintained at 50 °C and 80% relative humidity. Planks were considered "set" when they could support a 75 kg load without deforming. As shown in TABLE 13, both types of low-density CSH accelerated the setting time by about 80%.

TABLE 12

Formulation	Portland Cement	200 mesh Ground Silica	Cellulose Fiber	VFA	DA	Hollow Ceramic Spheres	Low-density CSH	Water ^a
K	38.5	25.7	9	1.5	0.3	25	0	54
L	35.5	23.7	9	1.5	0.3	25	5 ^b	54
M	35.5	23.7	9	1.5	0.3	25	5 ^c	54

Dry components by wt% of total dry weight. ^a Percent water added based on total weight of dry components to maintain consistent paste workability. ^b Low-density CSH of EXAMPLE 1. ^c Micro-cel® B low-density CSH.

TABLE 13

Formulation	Time to set (hrs)
K	35
L	6
M	6

EXAMPLE 7. Effect of low-density fiber cement on
after-die dimensional stability of fiber cement pastes

Extrudable fiber cement pastes were prepared in the manner of EXAMPLE 5, using the same ingredients. Low density CSH was substituted for cement and ground silica, maintaining a 6:4 ratio between cement and ground silica. Planks 89 mm wide by 25 mm thick were extruded from a Handlē laboratory extruder with a 75-mm barrel and allowed to set for 12 hours at 50 °C and 80% relative humidity. The planks were then autoclaved in saturated steam at 180 °C for 8 hours. The planks were cut into sections and the cross-sectional area of each section was measured. The percent increase for each cross-sectional area after autoclaving was determined. Results are tabulated in TABLE 13 as a function of low-density CSH content.

TABLE 14

Low-density CSH (wt%)	Increased cross-sectional area (%)
0	~15-20
1	8.4
2	6.5
3	5
4	6.5
5	6
10	~2

These results show that accelerating the setting time of the green fiber-cement paste has a beneficial effect on post-die swelling.

EXAMPLE 8. Effect of low-density CSH on
strength-to-weight ratio of extruded fiber cement

Fiber cement pastes of were prepared using the materials, except for the LD-CSH, and methods of EXAMPLE 5, according to TABLE 15.

TABLE 15

Formulation	Portland Cement	200-mesh Ground Silica	Cellulose Fiber	VFA	DA	Low-density CSH ^a	Water ^b
N	49.3	32.9	11	1.5	0.3	0	41.8
O	45.6	30.4	11	1.67	0.3	11	62.6
P	42.9	28.6	11	2.2	0.3	15	68.9
Q	39.9	26.85	11	2.25	0.3	20	83.5
R	33.1	22.1	11	3.5	0.3	30	116
S	27.5	18.3	11	3.92	0.3	50	144

Dry components by wt% of total dry weight. ^a Low-density CSH of EXAMPLE 1. ^b Percent water added based on total weight of dry components to make pastes of equivalent consistency and workability.

Once mixed and homogenized, each formulation was extruded through a rectangular die into planks 10 mm thick by 50 mm wide using a Hanble laboratory extruder with a 75 mm barrel. Planks of each formulation were cut from the extruded material as it exited the die, allowed to set for 12 hours, and cured in an autoclave at 180 °C steam for 12 hours. After curing, planks were cut into test specimens, measured, and weighed to determine the dry density (D) and placed in a MTS mechanical tester to determine ultimate tensile strength. Strength-to-weight ratio was determined by dividing ultimate tensile strength by the formulation density. As shown in TABLE 15, formulations using low-density CSH can attain higher strength-to-weight ratios than denser materials containing no low-density CSH. Low-density CSH content can be adjusted to maximize the strength to weight ratio of a given fiber cement formulation:

TABLE 15

Formulation	Density (g/cm ³)	Ultimate stress (MPa)/Density
N	1.28	5.65
O	1.08	7.32
P	1.00	6.27
Q	0.87	7.01
R	0.66	5.28
S	0.57	2.63

The embodiments illustrated and described above are provided as examples of certain preferred embodiments of the present invention. Various changes and modifications can be made to the embodiments presented herein by those skilled in the art without departure from the spirit and scope of this invention, the scope of which is limited only the claims appended hereto.

WHAT IS CLAIMED IS:

1. The use of a low density calcium silicate hydrate additive in a cementitious formulation for the purpose of accelerating the curing of the formulation as compared to an equivalent formulation made without low density calcium silicate hydrate.
2. In a method for extruding a cementitious article, the improvement comprising adding a quantity of low density calcium silicate hydrate to a formulation used to produce the article sufficient to accelerate the curing of the cementitious article as compared to an equivalent formulation made without low density calcium silicate hydrate.
3. In a method for forming a cementitious article, the improvement comprising adding a quantity of low density calcium silicate hydrate to a formulation used to produce the article sufficient to accelerate the curing of the cementitious article compared to an equivalent formulation made without low density calcium silicate hydrate.
4. A method of forming a cementitious material, comprising:
 - preparing a formulation comprising a cementitious binder and aggregate;
 - adding to the formulation a quantity of low density calcium silicate hydrate sufficient to reduce the curing time of the formulation as compared to an equivalent formulation without calcium silicate hydrate; and
 - curing the formulation for a time sufficient to cause the material to set;
wherein the formulation sets in a period of time that is at least 10% less than the time it would take an equivalent formulation without calcium silicate hydrate to set.
5. The method of Claim 4, wherein the formulation sets in a period of time that is at least 20% less than the time it would take an equivalent formulation without calcium silicate hydrate to set.
6. The method of Claim 4, wherein the low-density calcium silicate hydrate has a bulk density of between about 0.015 g/cm³ and 1.5 g/cm³.
7. The method of Claim 4, wherein the cementitious material comprises sufficient low-density calcium silicate hydrate to produce a cured product of density between about 0.6 g/cm³ and 1.2 g/cm³.
8. The method of Claim 4, comprising forming the material using the Hatschek production process.

9. The method of Claim 8, wherein preparing the formulation comprises mixing a slurry of cellulose fiber pulp with a slurry of silica to form a mixture, and adding cement to the mixture.

10. The method of Claim 9, wherein the calcium silicate hydrate is added as a slurry to the mixture.

11. The method of Claim 9, wherein the calcium silicate hydrate is added in dry form to the mixture.

12. The method of Claim 9, further comprising adding additional aggregates and additives to the mixture.

13. The method of Claim 4, comprising forming the material into articles for building and construction applications.

14. The method of Claim 13, wherein the material is formed into a concrete article.

15. The method of Claim 14, wherein preparing the formulation comprises making a mixture by adding cement, silica and aggregate into a mixing machine and dry mixing the mixture.

16. The method of Claim 15, further comprising adding fiber reinforcement to the mixture.

17. The method of Claim 16, wherein the fiber reinforcement is selected from the group consisting of steel wire, steel rods, poly-fiber and carbon fiber.

18. The method of Claim 15, wherein the silica is quartz sand.

19. The method of Claim 15, wherein the aggregate is selected from the group consisting of natural rock, sand, gravel, limestone and bottom ash.

20. The method of Claim 15, further comprising adding water to the mixture and mixing the mixture.

21. The method of Claim 20, wherein adding the calcium silicate hydrate accelerator to the formulation occurs after mixing the mixture with water.

22. The method of Claim 21, further comprising mixing the mixture having calcium silicate hydrate.

23. The method of Claim 14, wherein the low-density calcium silicate hydrate accelerator is added to the cementitious mixture after the cementitious mixture has been transported to its place of intended use

24. The method of Claim 4, wherein the formulation is formed into a green article by extrusion.

25. The method of Claim 24, wherein preparing the formulation comprises making a mixture by adding cement, silica, and fibers into a mixing machine, and dry mixing the mixture.

26. The method of Claim 25, wherein the formulation further comprises a siliceous aggregate in addition to the silica.

27. The method of Claim 24, wherein the fibers are selected from the group consisting of cellulose fibers, synthetic polymer fibers, and a combination of both.

28. The method of Claim 24, further comprising adding organic admixtures to the mixture.

29. The method of Claim 25, further comprising adding water to the mixture, and mixing the mixture with the water.

30. The method of Claim 29, wherein the calcium silicate hydrate is added to the mixture in dry form before adding water, and the calcium silicate hydrate is dry mixed with the mixture.

31. The method of Claim 25, wherein the calcium silicate hydrate is added to the mixture in slurry form after dry mixing the mixture.

32. The method of Claim 29, further comprising discharging the mixture into a kneader and kneading the mixture into a paste.

33. The method of Claim 32, wherein the paste is degassed under vacuum.

34. The method of Claim 32, wherein the paste is extruded through a die to form a green article.

35. The method of Claim 32, wherein the water-solid-ratio of the paste is between about 0.4 to 1.2.

36. The method of Claim 34, comprising precuring the mixture for a predetermined period of time.

37. The method of Claim 34, further comprising autoclaving the green article.

38. An accelerated-curing cementitious formulation comprising:
a cementitious binder;
an aggregate; and

a low-density calcium silicate hydrate accelerant selected to reduce the curing time of the formulation, wherein the low-density calcium silicate hydrate is added in a quantity sufficient to reduce the curing time of the formulation compared to an equivalent formulation made without low density calcium silicate hydrate.

39. The formulation of Claim 38, wherein the low-density calcium silicate hydrate accelerant has a bulk density of between about 0.015 g/cm³ and 1.5 g/cm³.

40. The formulation of Claim 38, comprising a quantity of the low-density calcium silicate hydrate accelerant sufficient to accelerate the curing of the formulation by about 10% or more compared to an equivalent formulation without low-density calcium silicate hydrate.

41. The formulation of Claim 38, comprising a quantity of the low-density calcium silicate hydrate accelerant sufficient to accelerate the curing of the formulation by about 50% or more compared to an equivalent formulation without low-density calcium silicate hydrate.

42. The formulation of Claim 38, comprising sufficient low-density calcium silicate hydrate accelerant to produce a product of density between about 0.6 g/cm³ and 1.2 g/cm³ wherein the strength-to-weight ratio of the product is higher compared to an equivalent product without low-density calcium silicate hydrate.

43. The formulation of Claim 42, wherein the formulation is used to make articles for building and construction applications.

44. The formulation of Claim 42, wherein the formulation is used in the Hatschek process.

45. The formulation of Claim 44, further comprising between about 5% and 15% cellulose fibers.

46. The formulation of Claim 44, comprising between about 0.5% and 15% low-density calcium silicate hydrate.

47. The formulation of Claim 44, comprising between about 25% and 50% Portland cement.

48. The formulation of Claim 44, comprising between about 25% and 50% silica.

49. The formulation of Claim 44, wherein the silica is ground to about 200-mesh.

50. The formulation of Claim 44, wherein the aggregate is silica, and further comprising between about 0% and 40% of an additional aggregate.

51. The formulation of Claim 50, wherein the additional aggregate is a siliceous aggregate.

52. The formulation of Claim 51, wherein the additional aggregate is selected from the group consisting of cenospheres, perlite, vermiculite, volcanic ash, fly ash and bottom ash.

53. The formulation of Claim 44, further comprising between about 0% and 5% additives.

54. The formulation of Claim 53, wherein the additives are selected from the group consisting of alumina, pigments, colorants, flocculants, drainage aids, silicone materials, clays, mica, wollastonite, calcium carbonate and fire retardants.

55. The formulation of Claim 38, wherein the formulation is made into an extrudable paste.

56. The formulation of Claim 55, comprising between about 2% and 20% low-density calcium silicate hydrate.

57. The formulation of Claim 55, comprising between about 5% and 15% low-density calcium silicate hydrate.

58. The formulation of Claim 55, comprising sufficient low-density calcium silicate hydrate accelerator to reduce post-die swelling to less than about 6.5% as measured by increase in cross-sectional area.

59. The formulation of Claim 55, comprising between about 15% and 60% Portland cement.

60. The formulation of Claim 55, comprising between about 0% and 60% silica.

61. The formulation of Claim 60, wherein the silica is 200-mesh ground silica.

62. The formulation of Claim 55, wherein the aggregate is silica, and further comprising between about 0% and 40% of an additional aggregate.

63. The formulation of Claim 62, wherein the additional aggregate is a siliceous aggregate.

64. The formulation of Claim 63, wherein the siliceous aggregate is selected from the group consisting of cenospheres, perlite, vermiculite, volcanic ash, fly ash and bottom ash.

65. The formulation of Claim 63, wherein the siliceous aggregate has a particle size between about 50 and 250 microns.
66. The formulation of Claim 55, further comprising between about 0% and 15% fibers.
67. The formulation of Claim 66, wherein the fibers are cellulose.
68. The formulation of Claim 66, wherein the fibers are synthetic.
69. The formulation of Claim 55, further comprising between about 0% and 2% additives.
70. The formulation of Claim 69, wherein the additives are selected from the group consisting of alumina, pigments, colorants, surfactants, silicone materials, clays, mica, wollastonite, calcium carbonate and fire retardants.
71. The formulation of Claim 55, further comprising between about 0.2% and 3% of a viscosity enhancing agent.
72. The formulation of Claim 71, wherein the viscosity enhancing agent is selected from the group consisting of methylcellulose, hydroxyethylcellulose, hydroxyethylmethylcellulose and hydroxypropylmethylcellulose.
73. The formulation of Claim 55, further comprising between about 0% and 2% of a water reducing agent.
74. The formulation of Claim 55, further comprising between about 0% and 1% of an aeration agent.
75. The formulation of Claim 38, wherein the formulation is used to make concrete.
76. The formulation of Claim 75, comprising between about 0.5% and 20% low-density calcium silicate hydrate.
77. The formulation of Claim 75, comprising a quantity of the low-density calcium silicate hydrate accelerator sufficient to accelerate the curing of the formulation by at least about 65% compared to an equivalent formulation without low-density calcium silicate hydrate.
78. The formulation of Claim 75, comprising between about 15% and 50% Portland cement.
79. The formulation of Claim 75, comprising between about 0% and 70% silica.
80. The formulation of Claim 79, wherein the silica is quartz sand.

81. The formulation of Claim 80, wherein the quartz sand has a particle size of about 100 to 400 microns.

82. The formulation of Claim 75, wherein the aggregate is silica, and further comprising between about 0% and 40% of an additional aggregate.

83. The formulation of Claim 82, wherein the additional aggregate is a siliceous aggregate.

84. The formulation of Claim 83, wherein the siliceous aggregate is selected from the group consisting of natural rock, sand, gravel, limestone and bottom ash..

85. The formulation of Claim 75, further comprising between about 0% and 15% fiber reinforcement.

86. The formulation of Claim 85, wherein the fiber reinforcement is selected from the group consisting of steel wire, steel rods, synthetic polymer -fiber and carbon fiber.

87. The formulation of Claim 75, further comprising between about 0% and 2% additives.

88. The formulation of Claim 87, wherein the additives include a viscosity enhancing agent.

89. The formulation of Claim 88, wherein the viscosity enhancing agent is selected from the group consisting of methylcellulose, hydroxyethylcellulose, hydroxyethylmethylcellulose and hydroxypropylmethylcellulose.

90. The formulation of Claim 75, further comprising between about 0% and 0.2% of a leveling agent.

91. The formulation of Claim 75, further comprising between about 0% and 2% of a water reducing agent.

92. The formulation of Claim 75, further comprising between about 0% and 1% of an aeration agent.

93. The formulation of Claim 75, further comprising water, and wherein the water-to-cement ratio in the formulation is between about 0.35 and 1.

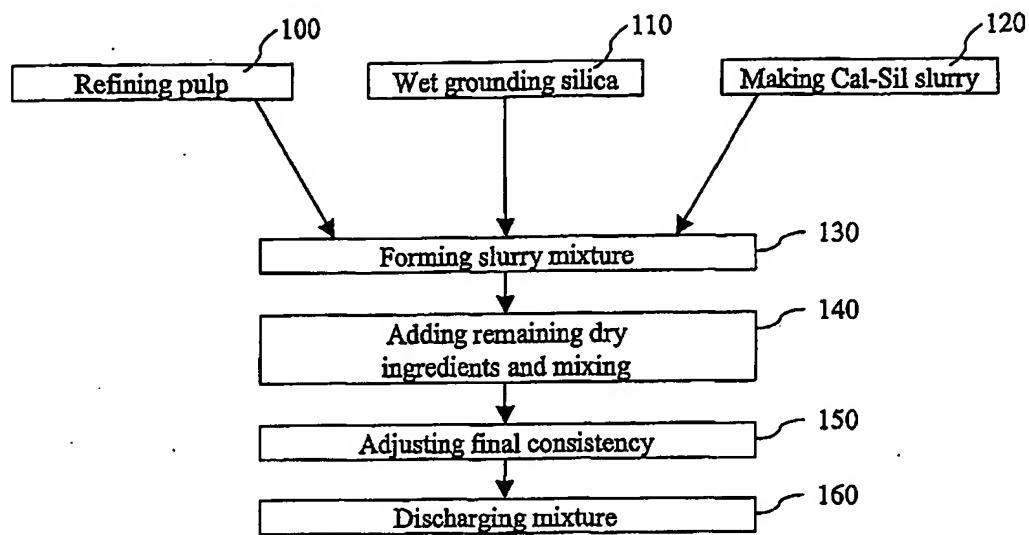


Figure 1

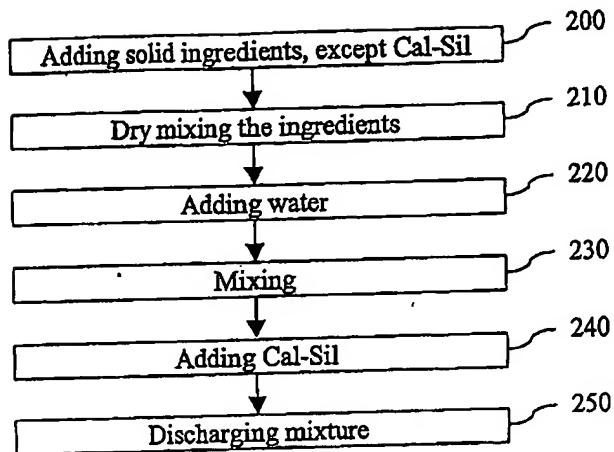


Figure 2

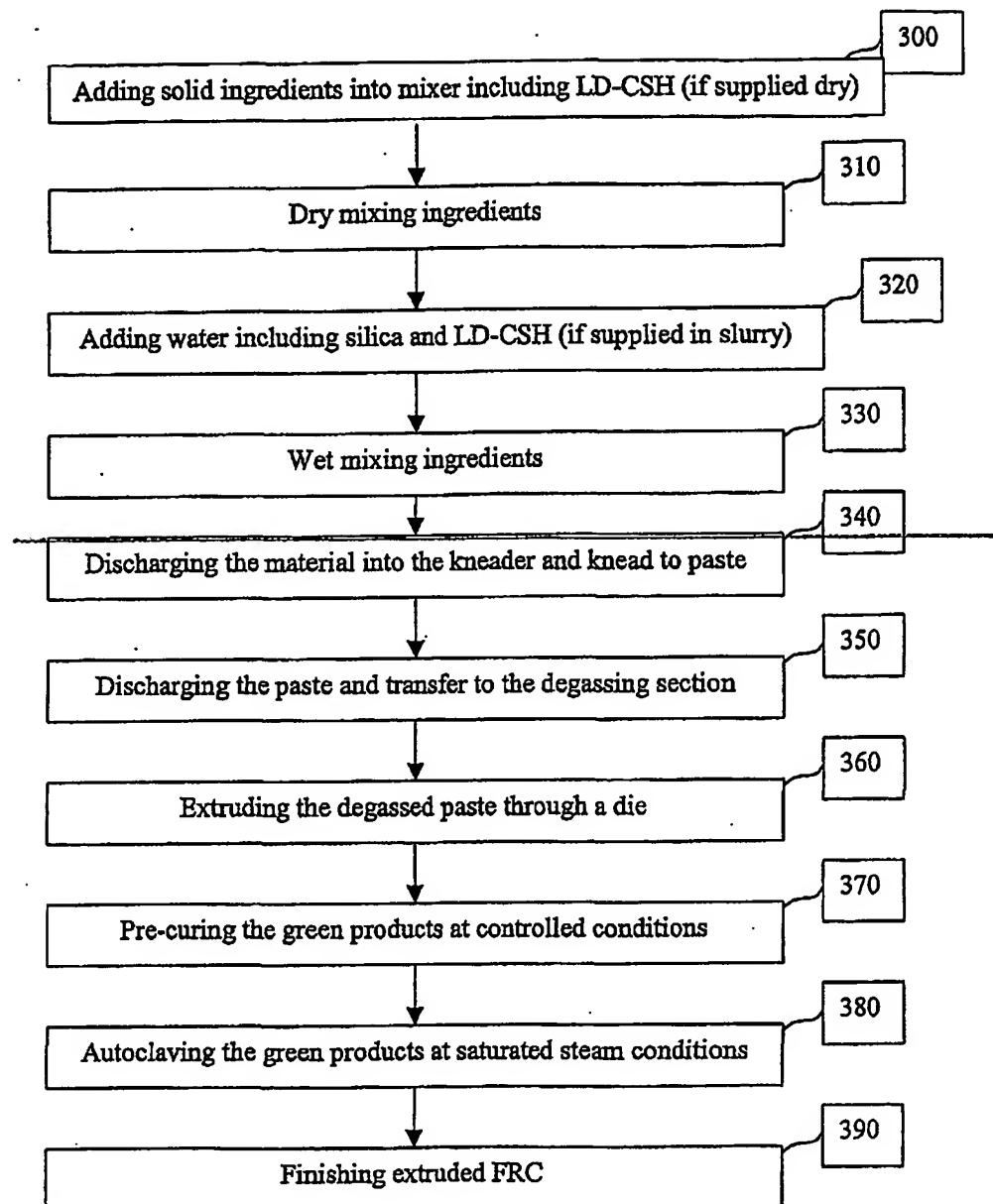


Figure 3

**Curing Behavior of Fiber Cement
Formulations Containing Low Density
CSH**

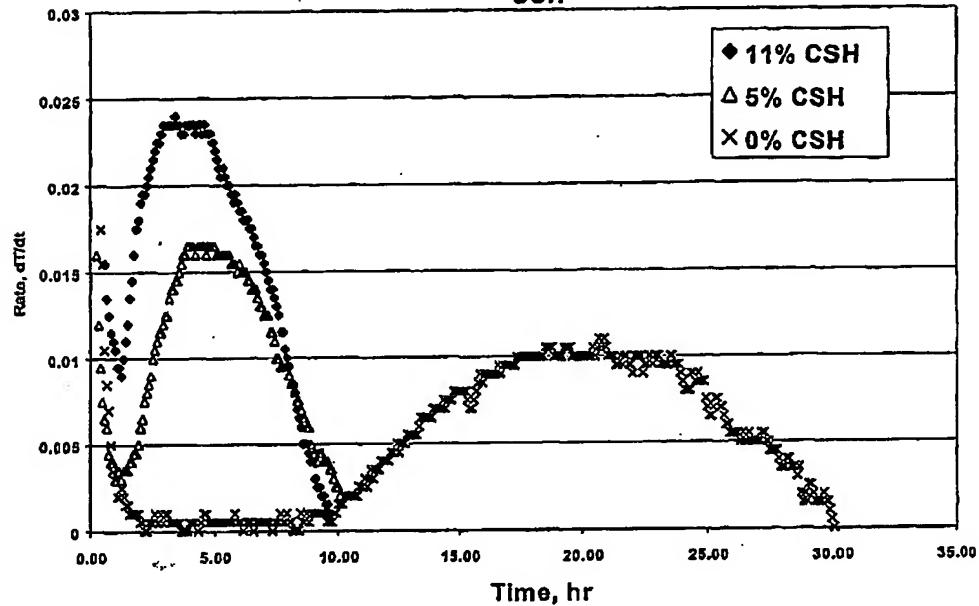


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB02/01833

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages.	Relevant to claim No.
Y	Derwent Abstracts 06-144944, Class L02, JP 6-144944 A (ASAHI KASEI KOGYO KK) 24 May 1994.	1-93
Y	US 4162924 A (K.K. OSAKA PACKING SEIZOSHO) 31 July 1972 See column 10 lines 34-39.	1-93
Y	US 5709743 A (LETURE et. al.) 20 January 1998, See examples, tables IX and X.	1-93
Y	US 5383967 A (CHASE) 24 January 1995. See column 3 line 64 - column 4 line 3.	1-93
Y	US 5372640 A (SCHWARZ) 13 December 1994. See column 6 line 62 - column 7 line 8.	1-93

INTERNATIONAL SEARCH REPORT

International application No. PCT/IB02/01833

A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: C04B 22/06, C04B 103;12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl. ⁷: C04B 22/06, C04B 103;12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent Online Abstracts and USPTO Internet site, C04b, B28b and E04c with keywords for set(ting) accelerators/enhancers and (hydrated) calcium silicate (hydrate), period 1975-2002.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X, Y	WO 01/68547 A (JAMES HARDIE RESEARCH PTY. LTD.) 20 September 2001 See whole document, especially examples.	1-93
X, Y	WO 00/21901 A (JAMES HARDIE RESEARCH PTY. LTD.) 20 April 2000 See whole document, especially examples.	1-93
X, Y	WO 98/45222 A (JAMES HARDIE RESEARCH PTY. LTD.) 15 October 1998 See whole document, especially examples.	1-93
X, Y	EP 417418 A (BAUSTOFFWERKE DÜRMERSHEIM GmbH) 6 July 1990 See whole document, especially examples.	1-93
Y	Derwent Abstracts Accession No. 97-480943/45, Class L02, CN 1120525 A (UNIV. HUNAN SCI & ENG.) 17 April 1996.	1-93

 Further documents are listed in the continuation of Box C See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
17 June 2002

Date of mailing of the international search report

24 JUN 2002

Name and mailing address of the ISA/AU
AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaaustralia.gov.au
Facsimile No. (02) 6285 3929

Authorized officer

GRAEME J. BROXAM

Telephone No : (02) 6283 2133

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB02/01833

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member			
WO	200168547	AU	50832/2001	US	2001047741	
WO	200021901	AU	11373/2000			
WO	9845222	AU	69111/98	EP	973699	NZ 500215
		US	6346146	ZA	9803063	
EP	417418	DD	300637	DE	3930458	
US	4162924	BR	7700875	CA	1106142	DE 2705828
		GB	1539141	JP	52-098021	AU 22154/77
		JP	53-146997			
JP	06-144944	JP	06-144944			
CN	1120525	NONE				
US	5709743	CA	2168253	EP	711259	FR 2708592
		WO	95/04007			
US	5383967	AU	17626/92	WO	92/17413	
US	5372640	AU	83382/91	CA	2072646	CH 682561
		CS	9102699	EP	500840	ES 2033585
		GB	2247454	HU	9201327	MZ 9100900
		NO	921713	WO	92/04299	WO 92/04300
		BR	9104672			